Chemical Evolution of Groundwater Near a Sinkhole Lake, Northern Florida: 1. Flow Patterns, Age of Groundwater, and Influence of Lake Water Leakage

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Chemical evolution of groundwater near a sinkhole lake, northern Florida

1. Flow patterns, age of groundwater, and influence of lake water leakage

Brian G. Katz

U.S. Geological Survey, Tallahassee, Florida

Terrie M. Lee

U.S. Geological Survey, Tampa, Florida

L. Niel Plummer and Eurybiades Busenberg

U.S. Geological Survey, Reston, Virginia

Abstract. Leakage from sinkhole lakes significantly influences recharge to the Upper Floridan aquifer in poorly confined sediments in northern Florida. Environmental isotopes (oxygen 18, deuterium, and tritium), chlorofluorocarbons (CFCs: CFC-11, CCl_3F; CFC-12, CCl_2F_2; and CFC-113, $C_2Cl_3F_3$), and solute tracers were used to investigate groundwater flow patterns near Lake Barco, a seepage lake in a mantled karst setting in northern Florida. Stable isotope data indicated that the groundwater downgradient from the lake contained 11–67% lake water leakage, with a limit of detection of lake water in groundwater of 4.3%. The mixing fractions of lake water leakage, which passed through organic-rich sediments in the lake bottom, were directly proportional to the observed methane concentrations and increased with depth in the groundwater flow system. In aerobic groundwater upgradient from Lake Barco, CFC-modeled recharge dates ranged from 1987 near the water table to the mid 1970s for water collected at a depth of 30 m below the water table. CFC-modeled recharge dates (based on CFC-12) for anaerobic groundwater downgradient from the lake ranged from the late 1950s to the mid 1970s and were consistent with tritium data. CFC-modeled recharge dates based on CFC-11 indicated preferential microbial degradation in anoxic waters. Vertical hydraulic conductivities, calculated using CFC-12 modeled recharge dates and Darcy's law, were 0.17, 0.033, and 0.019 m/d for the surficial aquifer, intermediate confining unit, and lake sediments, respectively. These conductivities agreed closely with those used in the calibration of a three-dimensional groundwater flow model for transient and steady state flow conditions.

Introduction

Solution lakes form in northern Florida as a result of dissolution of underlying limestone followed by infilling of solution features (e.g., cavities or channels) by overlying unconsolidated silicate material [*Arrington and Lindquist*, 1987]. The infilling material can be highly conductive hydraulically [*Lee and Swancar*, 1995] and can serve as an effective conduit for direct recharge to the Upper Floridan aquifer (UFA). Little is known of the effect of subsurface outflow or lake water leakage from solution lakes on recharge processes and on the chemistry of groundwater downgradient from these lakes. Leakage of lake water through organic-rich sediments in the bottom of these lakes could have a profound impact on the quality of water in the UFA, the source of public water supply in most of the northern peninsula of Florida.

The importance of groundwater inflow to the hydrochemical

budgets of solution lakes has received considerable attention recently because of the influence of groundwater inflow on the regulation of the acid-neutralizing capacity of these lakes [*Baker et al.*, 1988; *Pollman and Canfield*, 1991; *Stauffer and Canfield*, 1992]. Groundwater seepage can be a significant input to solution lakes because of porous soils, high water table, and lack of surface water inlets or outlets along the ridge and upland areas of Florida [*Fellows and Brezonik*, 1980; *Belanger and Walker*, 1990; *Pollman et al.*, 1991]. In contrast, no studies have made systematic measurements of the chemistry of groundwater downgradient from sinkhole lakes to evaluate the hydrochemical influence of subsurface outflow or lake water leakage.

Fundamental to the understanding of the chemical evolution of groundwater in these complex karstic flow systems is an accurate delineation of flow patterns and the determination of the origin and age of waters. In nonkarst settings, the interaction of groundwater and lake water systems has been investigated using hydraulic analyses [e.g., *Winter*, 1976, 1983; *Winter et al.*, 1988; *Sacks et al.*, 1992a] and hydrologic tracers, such as oxygen 18 and deuterium [e.g., *Gonfiantini*, 1986; *Krabbenhoft*
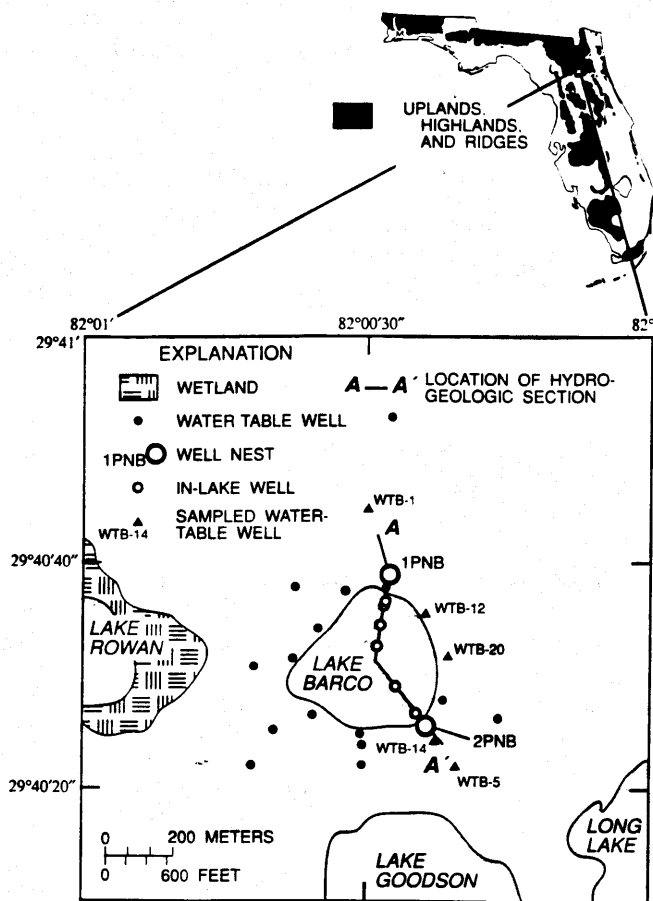
Figure 1. Lake Barco study area, showing location of observation wells and trace of hydrogeologic section.

et al., 1990], tritium [*Gilath and Gonfiantini*, 1983], and inorganic constituents released by weathering [*Stauffer*, 1985; *Kenoyer and Bowser*, 1992]. Recently, anthropogenic organic compounds, such as chlorofluorocarbons have been used successfully to date shallow groundwaters, estimate rates of groundwater movement, and investigate the interaction between groundwater and surface water [*Busenberg and Plummer*, 1992; *Phillips et al.*, 1992; *Plummer et al.*, 1993; *Dunkle et al.*, 1993].

This study investigates the interaction between groundwater and a sinkhole lake in northern Florida. Environmental isotopes, solute tracers, and chlorofluorocarbons (CFCs) provide considerable insight into flow patterns, sources and rates of recharge to groundwater, and the influence of lake leakage on the chemical evolution of groundwater. Rates of groundwater movement and vertical hydraulic conductivity determined from age dating of groundwater (CFCs and tritium) and numerical simulation techniques are compared. Integration of these two independent techniques can lead to an improved conceptual understanding of the interaction between groundwater and surface water [*Reilly et al.*, 1994]. This research is presented in two companion papers. This paper (paper 1) uses environmental tracers including tritium, stable isotopes, and CFCs and numerical simulation to investigate the impact of sinkhole lakes on the hydrology of the UFA and overlying aquifers. Paper 2 [*Katz et al.*, this issue] quantifies the geochemical reactions occurring as lake water leakage passes through organic-rich sediments in the lake bottom and recharges the

UFA. Knowledge of the interaction of shallow groundwater and lake water in karst areas and associated recharge processes will help in better understanding the susceptibility of poorly confined aquifer systems, such as the UFA, to contamination from natural and anthropogenic sources.

Site Description and Hydrogeologic Setting

Lake Barco is located in north central Florida, about 31 km east of Gainesville, Florida (Figure 1). The lake basin lies within the Katharine Ordway Preserve where no development is permitted. Lake Barco is an acidic seepage lake typical of other seepage lakes along ridges, uplands, and highlands in Florida which have no surface water inflow or outflow. The northern side of Lake Barco is surrounded by a ridge approximately 47 m above sea level, whereas the southern side of the lake has considerably less relief. The lake surface area is 12 ha, and average depth is about 4 m.

The Lake Barco catchment is in the Interlachen Sand Hills part of the Central Lake physiographic district [*Brooks*, 1981]. This district is characterized by the formation of active sinkholes. The numerous lakes and other surficial depressions in this region have formed as the result of the filling of solution voids in the underlying limestone by unconsolidated sediments [*Lane*, 1986]. Lake Barco is considered to be a cover collapse sinkhole, which is typical of many of the lakes in the Central Lake district [*Sinclair and Stewart*, 1985; *Arrington and Lindquist*, 1987]. The surficial sand deposits are hydraulically connected to the underlying carbonate rocks in most of the Interlachen Sand Hills region [*Brooks*, 1981]. Ground-penetrating radar (GPR) and seismic reflection surveys provided direct evidence of karst features and downwarping of beds within the surficial deposits in the Lake Barco basin [*Sacks et al.*, 1992b].

The hydrogeologic framework of the Lake Barco study area is shown in a cross section through the basin (Figure 2). Limestone of the Ocala Group of Upper Eocene age is unconformably overlain by 15–30 m of the Hawthorn Group of Miocene age, which consists of a variable mixture of sand, gravel, clay, phosphate, and carbonate sediments [*Scott*, 1988]. Distinct formations have not been delineated; however, the intermediate confining unit within the Hawthorn Group is probably breached in places [*Sacks et al.*, 1992b]. Undifferentiated sur-
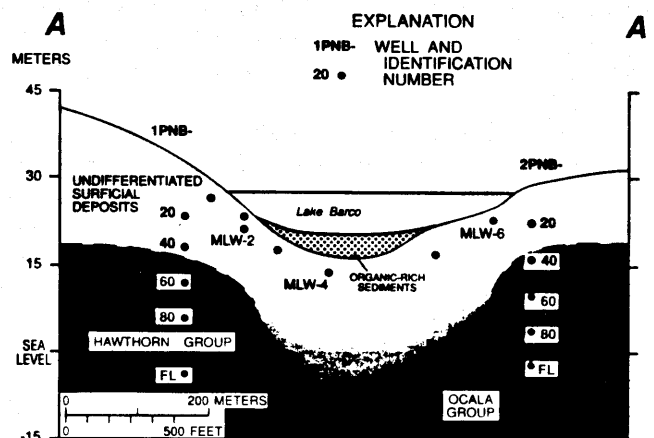

Figure 2. Generalized hydrogeologic section of the Lake Barco study area with the location of sampling sites in the 1PNB and 2PNB well nests (trace of section in Figure 1).

Table 1. Description of Observation Wells Sampled in the Lake Barco Study Area

Well Name	Latitude/Longitude	Well Depth Below Land Surface, m	Depth of Screened Interval Below Land Surface, m	Drilling Method
		Nested Wells		
1PNB-20	29°40'42"/82°00'29"	6.49	5.73–6.49	A
1PNB-40	29°40'42"/82°00'29"	12.1	11.3–12.1	A
1PNB-60	29°40'42"/82°00'29"	19.3	18.5–19.1	A
1PNB-80	29°40'42"/82°00'29"	24.2	23.4–24.2	A
1PNB-FL	29°40'42"/82°00'29"	37.2	33.5–37.2	R
2PNB-20	29°40'27"/82°00'25"	6.40	5.64–6.40	A
2PNB-40	29°40'27"/82°00'25"	12.3	11.6–12.3	A
2PNB-60	29°40'27"/82°00'25"	18.6	17.8–18.6	A
2PNB-80	29°40'27"/82°00'25"	24.9	24.1–24.9	A
2PNB-FL	29°40'27"/82°00'25"	31.4	29.8–31.4	R
		In-Lake Wells		
MLW-2	29°40'39"/82°00'31"	2.90*	2.23–2.90	D
MLW-4	29°40'33"/82°00'31"	4.05*	3.38–4.05	D
MLW-6	29°40'28"/82°00'27"	2.29*	1.62–2.29	D
		Water Table Wells		
WTB-1	29°40'47"/82°00'30"	13.6	12.1–13.6	A
WTB-5	29°40'24"/82°00'20"	8.93	7.41–8.93	A
WTB-12	29°40'39"/82°00'24"	3.60	2.08–3.60	A
WTB-14	29°40'26"/82°00'24"	6.68	5.16–6.68	A
WTB-20	29°40'35"/82°00'24"	6.98	5.46–6.98	A

All wells are 5 cm in diameter and screened except 1PNB-FL, which is 10 cm in diameter and has an open hole. Drilling method: A, auger; R, rotary; D, driven and jetted.
*Depth below lake bottom

ficial deposits of Holocene to Pliocene age lie above the Hawthorn Group and consists of poorly to well sorted sands with variable amounts of silt and clay. Seismic reflection data indicated that the Hawthorn Group and surficial deposits below the lake do not consist of coherent, continuous beds [*Sacks et al.*, 1992b]. Most likely, these beds are broken up because of subsidence activity and the concomitant infilling of solution voids in the limestone.

More than 3 m of soft, organic-rich sediments were measured at the bottom of the central part of the lake [*Sacks et al.*, 1992b]. The northern half of the lake has considerably more sediments than the southern half of the lake because of the steeper slope of the northern lake bed [*Sacks et al.*, 1992b]. The organic matter content (determined by loss on ignition at 550°C) ranged from 23 to 35% for sediments collected from depths of 0.25–12 cm below the sediment-water interface [*Norton et al.*, 1992]. The age of the lake is estimated to be at least 1000 years, based on the thickness of the sediments and estimates of recent sediment deposition rates [*Sacks et al.*, 1992b].

Soils in the lake basin are acidic, with pH values ranging from 4.5 to 5.0 (1:1 soil/water slurry), and consist predominantly of fine sand (0.25–0.1 mm) with low amounts of silt and clay-sized particles [*Readle*, 1990]. Saturated hydraulic conductivities and bulk densities range from 28.3 to 46 cm/h and 1.3 to 1.55 g/cm^3, respectively. This soil type typically has low amounts of extractable bases (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$), 0.04–0.27 meq/100 g soil with a base saturation of 4–9%; and low organic carbon content, 0.05–1.28%. The soil particles also have low amounts of citrate-dithionite extractable [*McKeague et al.*, 1971] iron (0.08%) and aluminum (0.03%), and the predominant clay minerals in decreasing order of abundance were an unidentified 14-Å intergrade, kaolinite, and smectite [*Readle*, 1990].

Methods

Groundwater and Lake Water Sampling

Water table and nested wells were installed in the Lake Barco basin in 1988 to monitor the areal and vertical distribution of hydraulic head as part of a study to compute the hydrologic budget of Lake Barco and to investigate the factors influencing the acid-neutralizing capacity in Lake Barco [*Pollman et al.*, 1991; *Sacks et al.*, 1992b; *Lee*, 1995]. Wells were screened near the water table and at depths of 1–30 m below the water table. Pertinent information on the depth below land surface and construction of selected wells is given in Table 1.

During the May 1991 and October 1991 sampling, the shallow nested wells (less than 18 m depth below land surface), in-lake wells, and lake water of 1 m depth were sampled using a peristaltic pump with silicone rubber and Tygon tubing. The deeper wells (greater than 18 m depth below land surface) were sampled using a helical rotor submersible (Keck or Fultz) pump with 0.95-cm Teflon discharge line at pumping rates of approximately 4 L/min. (The use of brand, firm, or trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.) The wells were purged with the pump positioned approximately 1–2 m above the screened interval, and the pump was subsequently lowered into the screened interval or open hole interval for sampling.

During the August-September 1992 sampling, water from all wells with the exception of the in-lake wells was collected using copper tubing (refrigeration grade) connected to a positive displacement gas-driven piston pump. Two main advantages of the gas-driven piston pump were the elimination of contamination by CFCs from the sampling equipment and the ability to set variable pumping rates of approximately 0.4–4 L/min. Due
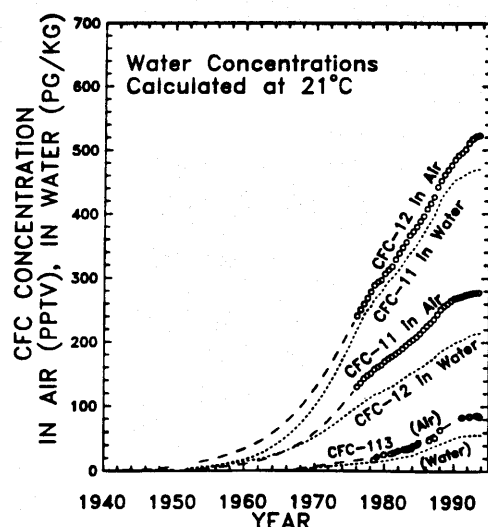
Figure 3. Concentrations of CFC-11, CFC-12, and CFC-113 in the atmosphere, and in water at 21°C, 1940–1993.

to the low specific capacity of most of the sampled wells, the low pumping rates were necessary to prevent drawdown of water in the casing from falling below the bottom of the well screen during pumping. Water samples from the lake and the in-lake wells were collected using copper tubing connected to a peristaltic pump.

Depending on the amount of stagnant water in the well casing and the pump rate, wells were purged for a period of at least 15–180 min, the time necessary to clear at least 3 casing volumes. Samples were taken only after the pH, specific conductance, temperature, and dissolved oxygen of the water had stabilized [*Wood*, 1976].

Rainfall Sampling

Rainfall (wet fall) was measured continuously onsite with a Belfort weighing bucket rain gage. Continuous measurements of the quantity of rainfall at the Lake Barco site began on April 29, 1989 [*Pollman et al.*, 1991]. The chemical and isotopic composition of rainfall (wet fall only) was collected onsite using two Aerochemetrics 301 wet/dry collectors. Weekly samples were analyzed for major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and NO_3^-) by Environmental Science and Engineering, Inc., in Gainesville, Florida. Specific conductance and pH were measured in the field and at the laboratory. Dry deposition for Florida was estimated based on wet/dry deposition ratios determined by *Baker* [1991] from dry bucket and ambient aerosol measurements. Three-month composite samples of rainfall were prepared for isotopic analysis (oxygen 18, deuterium, and sulfur 34) by volume weighting weekly samples from the second wet/dry collector. One-month composite samples of rainfall were prepared from weekly samples for the analysis of tritium.

Stable Isotopes and Tritium

The stable isotopes, oxygen 18 (^{18}O), and deuterium (^2H) were determined in precipitation, groundwater, and lake water to identify water sources and quantify mixing proportions [*Gonfiantini*, 1981]. Oxygen and hydrogen isotope results are reported in per mil relative to VSMOW (Vienna standard mean ocean water) and normalized on scales such that the oxygen and hydrogen isotopic values of SLAP (standard light

Antarctic precipitation) are $-55.5\%o$ and $-428\%o$, respectively [*Coplen*, 1988; *Coplen et al.*, 1991]. The 2σ precision of oxygen and hydrogen isotope results is 0.2 and 1.5%, respectively.

Tritium (^3H) has been used to evaluate consistency among CFC-modeled recharge dates by comparing measured ^3H concentrations in groundwater with the long-term ^3H input function of rainfall measured at the International Atomic Energy Agency (IAEA) precipitation monitoring station in Ocala, Florida [*Michel*, 1989]. Water samples for ^3H were collected and analyzed according to methods presented by *Michel* [1989]. Tritium activity is reported in tritium units (TU; 1 TU is equal to one ^3H atom in 10^{18} hydrogen atoms and 7.1 disintegrations per minute per gram of water) with a 1σ precision of less than 10% for waters containing more than 2 TU.

Chlorofluorocarbon Age-Dating Technique

The stability of CFCs, in particular trichlorofluoromethane (CCl_3F, CFC-11), dichlorodifluoromethane (CCl_2F_2, CFC-12), and trichlorotrifluoroethane ($C_2Cl_3F_3$, CFC-113), in the hydrosphere has led to their effective use as conservative tracers to age date groundwater that has been recharged during the past 50 years [*Plummer et al.*, 1993]. CFC-modeled recharge dates (as defined by *Busenberg and Plummer* [1992]) are determined on the basis of the equilibrium partitioning between rainwater and the partial pressures of these compounds in the troposphere or soil atmosphere.

The CFC-modeled date of recharge to groundwater is determined separately from the measured concentrations of CFC-11, CFC-12, and CFC-113 in solution by comparison of calculated equilibrium partial pressures, using CFC solubility data of *Warner and Weiss* [1985] and *Bu and Warner* [1995], with the respective atmospheric growth curve (Figure 3). Three independent dates are derived and can be used as a cross-check on the sampling and analytical methods. The current detection limit of less than 1 pg/kg for these compounds provides the capability to date groundwaters back to approximately 1948 with CFC-11, 1944 with CFC-12, and 1966 with CFC-113.

The method for the determination of a valid CFC-modeled recharge date is based on four implicit assumptions: (1) the partial pressures of CFCs are the same in both the soil (unsaturated zone) and the tropospheric atmospheres, which is valid for unsaturated zones less than 10 m in thickness [*Weeks et al.*, 1982], (2) the aquifer has not been contaminated by local, near-surface sources of CFCs commonly found near or in urban areas, (3) the CFC concentration in recharge water is in equilibrium with the CFC partial pressure in the soil atmosphere, and (4) the CFC concentrations in the aquifer have not been altered by biological, geochemical, or hydrologic processes.

The concentration of CFCs in groundwater is controlled by the atmospheric partial pressures and the temperature at the base of the unsaturated zone during recharge. The temperature at the time of recharge to groundwater, which is needed to define the Henry's law solubility constants, is defined as the temperature at the bottom of the unsaturated zone where equilibration can occur between CFCs in the unsaturated zone atmosphere and water infiltrating through this zone. Recharge temperatures for water from the surficial aquifer, the intermediate confining unit, and the UFA were determined on the basis of mean annual air temperature, measured groundwater temperature, and analyses of dissolved argon and nitrogen

gases. Argon and nitrogen gases are incorporated into recharge water in a similar manner to the dissolution of CFCs and their equilibrium solubilities can be determined using Henry's law [*Weiss*, 1970; *Wilhelm et al.*, 1977]. The dissolved-gas composition in the unsaturated zone typically is preserved in groundwater below the water table [*Heaton et al.*, 1981, 1983, 1986; *Podosek et al.*, 1980; *Busenberg et al.*, 1993]. The sampling apparatus, method of sample collection, and analytical procedure are described in detail by *Busenberg et al.* [1993] and *Katz* [1993].

The sampling apparatus and procedures described by *Busenberg and Plummer* [1992] were used to collect water samples for analysis of the CFCs. This method prevents contact of the water sample with the atmosphere. The sampling apparatus was connected to the pump using 0.6-cm aluminum tubing. A water sample volume of 62 mL was collected in a borosilicate-glass ampule that was flame sealed in the field for subsequent transport and storage in the laboratory until analysis. Typically, six ampules of water were collected at each site. The pH, specific conductance, dissolved oxygen, and temperature of the water were monitored throughout the sampling period at 5-min intervals. Three to six of the CFC samples collected at each site were analyzed in the laboratory for CFC-11, CFC-12, and CFC-113 using a purge-and-trap gas chromatography technique with an electron capture detector. Calibration and measurement procedures and a detailed description of the technique are given by *Busenberg and Plummer* [1992].

Groundwater Flow Patterns

Hydraulic Head Data

Water levels in the wells near Lake Barco declined from 1989 through 1990 because of below normal rainfall during 1989 and 1990 [*Sacks et al.*, 1992b]. Groundwater levels and lake stage began to increase after increased amounts of rainfall during 1991 and 1992. Water table gradients (Figure 4) and vertical head values (Figure 5) for October 9–10, 1991, generally are representative of conditions observed during May 1991
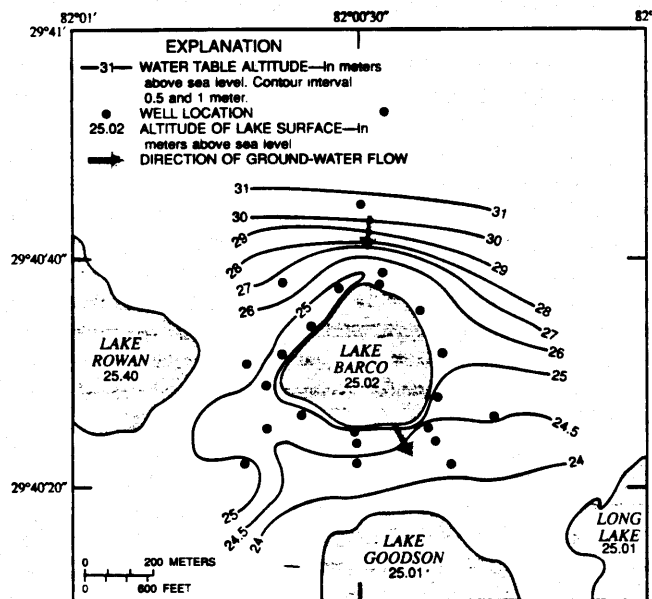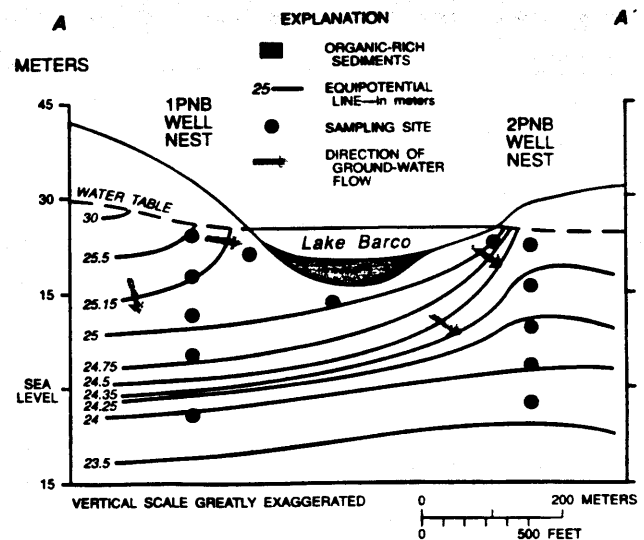

Figure 5. Vertical hydraulic head distribution and direction of groundwater flow with depth, October 9–10, 1991.

Figure 4. Configuration of the water table and direction of shallow groundwater flow, October 9–10, 1991.

to August 1992. Head values were typically higher on the northern half of Lake Barco, the apparent inflow side of the lake. However, groundwater inflow occurs only along the northeast perimeter of the lake (near the 1PNB site) for approximately 12% of the total circumference of the lake [*Pollman et al.*, 1991]. The remaining groundwater that moves laterally toward the lake, but does not contribute inflow, flows beneath Lake Barco where it mixes with leakage through the lake bottom. North of the lake near the 1PNB site the direction of groundwater flow is predominantly downward, with a small component of shallow groundwater entering the lake (Figure 5). During average recharge conditions, *Lee* [1995] estimates that groundwater inflow to the lake contributes about 9–18% of the total inflow to the lake (groundwater plus direct rainfall on the lake surface); however, during the drier period of May 1989 through December 1990, groundwater contributed only 1–10% of the total inflow to Lake Barco.

Lake Barco loses water to the surficial aquifer along the lake's southern side, as evidenced by the lower elevation of the water table along the entire southern perimeter of the lake, especially in the vicinity of well nest 2PNB (Figure 4). Groundwater flow is laterally downward at the 2PNB site, as a result of the strong downward head gradient (Figure 5). A depressional feature in the limestone surface offshore from site 2PNB and the presence of a highly conductive sand lens above the limestone at site 2PNB [*Sacks et al.*, 1992b] have resulted in poor confinement of the UFA in this area. Lateral flow occurs from Lake Barco toward Lake Goodson and Long Lake, each of which are at lower altitudes (Figure 4).

Leakage from Lake Barco to the underlying surficial aquifer and UFA contributes significantly to the total lake outflow. During a 20-month period of hydrologic budget measurements (May 1989 to December 1990), lake water leakage contributed 29% of the total outflow (leakage plus evapotranspiration) and exceeded groundwater inflow to the lake by a factor of 10–15 [*Lee*, 1995]. During 1991–1992, leakage from the lake was indicated by a relatively constant downward head difference (1.07–1.28 m) between the lake and the UFA, as measured in well 1PNB-FL. Water levels in the in-lake wells were essentially equal to the lake level during the sampling period (May

Table 2. Oxygen 18 and Deuterium Content of Groundwater, Rainfall, and Lake Water

Site Name	Date of Sample	$\delta^{18}O$, ‰	δD, ‰
1PNB-20	May 10, 1991	−4.20	−21.5
	Oct. 9, 1991	−3.85	−18.0
	Sept. 1, 1992	−4.40	−24.5
1PNB-40	May 10, 1991	−3.75	−17.5
	Oct. 9, 1991	−3.55	−17.0
	Aug. 31, 1992	−4.10	−21.0
1PNB-60	May 11, 1991	−3.80	−17.5
	Oct. 9, 1991	−3.65	−18.0
	Aug. 31, 1992	−3.95	−19.5
1PNB-80	Oct. 10, 1991	−3.60	−18.5
1PNB-FL	May 11, 1991	−3.85	−18.0
	Oct. 9, 1991	−3.60	−18.0
	Aug. 31, 1992	−3.95	−20.0
2PNB-20	May 11, 1991	−2.60	−12.5
	Oct. 9, 1991	−2.35	−11.5
	Sept. 2, 1992	−2.25	−11.0
2PNB-40	May 12, 1991	−0.45	−1.5
	Oct. 9, 1991	−0.35	−0.5
	Sept. 2, 1992	−1.00	−5.5
2PNB-60	Sept. 2, 1992	+0.25	−2.5
2PNB-80	May 12, 1991	−0.45	−2.0
	Oct. 9, 1991	−0.45	−3.0
	Sept. 1, 1992	−0.45	−2.0
2PNB-FL	May 12, 1991	+0.50	+2.0
	Oct. 9, 1991	+0.60	+3.0
	Sept. 1, 1992	+0.85	+2.0
MLW-2	May 11, 1991	−3.75	−18.0
	Oct. 9, 1991	−3.65	−16.0
	Sept. 3, 1992	−3.85	−19.0
MLW-4	May 11, 1991	+0.90	+3.0
	Oct. 10, 1991	+1.20	+5.5
	Sept. 3, 1992	+0.95	+2.5
MLW-6	May 11, 1991	−3.55	−16.5
	Oct. 9, 1991	−3.35	−14.5
	Sept. 4, 1992	−3.35	−15.5
Rainfall	April 2 to July 2, 1991	−3.05	−14.0
	July 2 to Oct. 8, 1991	−3.30	−15.5
	Oct. 8 to Dec. 31, 1991	−3.01	−12.5
	Jan. 1 to March 31, 1992	−3.60	−16.0
	March 31 to June 30, 1992	−4.15	−22.0
	June 30 to Sept. 29, 1992	−3.35	−15.5
Lake Barco	Nov. 6, 1990	+4.60	+22.0
	Dec. 4, 1990	+4.65	+21.5
	March 5, 1991	+4.10	+19.0
	May 11, 1991	+4.10	+20.0
	Oct. 10, 1991	+3.90	+19.0
	Dec. 31, 1991	+4.25	+20.5
	Feb. 28, 1992	+3.80	+17.5
	April 30, 1992	+4.35	+21.0
	July 29, 1992	+4.65	+21.0
	Sept. 3, 1992	+3.60	+16.5
WTB-1	Oct. 9, 1991	−4.15	−24.5
WTB-5	Oct. 9, 1991	−4.05	−17.5
WTB-14	Oct. 9, 1991	−3.5	−16.5
WTB-20	May 11, 1991	−3.70	−18.0

1991 to September 1992) and during 1988 through 1990 [*Sacks et al.*, 1992b]. In-lake well 4 (MLW-4) generally had a measurable head difference, usually less than 3.5 cm lower than the lake stage. Unfortunately, the in-lake wells did not provide reliable head measurements, because of possible leakage of lake water at casing joints [*Sacks et al.*, 1992b].

Stable Isotope Data

Sources of water. Deuterium and oxygen 18 in groundwater, rainfall, and lake water were used to determine flow patterns near Lake Barco and mixing processes in the groundwater flow system. The isotopic compositions of rainfall (three-month composite samples collected during April 1991 to September 1992) and groundwater upgradient of Lake Barco are similar (Table 2), and, because they plot along the meteoric water line (MWL) [*Craig*, 1961], are probably little affected by evaporation (Figure 6). The upgradient groundwaters are slightly depleted relative to the average composite rainfall, indicating that recharge occurs primarily in the late winter to early spring months.

Estimates of recharge rates based on mean chloride concentrations in shallow groundwater and rainfall ranged from 14.9 to 39.4 cm/yr, as determined from the relation [*Edmunds et al.*, 1992]

$$R_d = P(C_p/C_s), \qquad (1)$$

where R_d is the recharge rate in centimeters per year, P is the mean annual rainfall in centimeters per year, C_p is the mean volume-weighted chloride concentration in rainfall; and C_s is the mean chloride concentration in shallow groundwater. These values of recharge compare favorably with estimates of 2.5–25 cm/yr using a regional approach that combined qualitative information with quantitative groundwater flow modeling [*Aucott*, 1988].

Lake Barco has a distinctly different isotopic composition than rainfall or upgradient groundwater (Figure 6). Evaporation of lake water has caused substantial enrichment in δ^2H and $\delta^{18}O$ [e.g., *Gilath and Gonfiantini*, 1983]. The isotopic composition of lake water remained remarkably constant during the period November 1990 to September 1992 (Table 2), with a mean and standard deviation for $\delta^{18}O$ and δ^2H of +4.2 ± 0.3‰ and 19.8 ± 1.7‰, respectively. Lake water samples were collected for stable isotopic composition at 1 m depth below the lake surface and were assumed to be representative of the isotopic composition of the lake, both vertically and spatially. This assumption is based on a previous study during 1988 to 1990, when Lake Barco did not thermally stratify and daily mean lake temperatures varied by less than 1°C from the surface to the bottom of the lake [*Sacks et al.*, 1992b].

Water samples from two in-lake wells, MLW-2 and MLW-6 (Figure 2) have isotopic compositions similar to meteoric water and plot along the MWL (Figure 6). Both wells were installed in 1988, when the lake had a larger surface area than during subsequent sampling in 1991–1992. As a result of below-normal rainfall the lake stage declined 2.1 m during 1988–1990, and the lake volume decreased by 45% [*Sacks et al.*, 1992b]. From 1988 through 1990, MLW-2 was upgradient from the lake, whereas MLW-6 was originally downgradient from the lake. The isotopic composition of water from MLW-2 indicates that groundwater inflow to the lake still (1992) occurs at this site; however, the stable isotope data indicate that a gradient reversal has occurred at the MLW-6 site, most likely as a result of transient water table mounding on the downgradient side of the lake. Water from the MLW-6 site likely flowed into the lake as a result of the lower lake stage. Stable isotopes ($\delta^{18}O$ and δ^2H) indicate that a hinge line [*Cherkauer and Zager*, 1989] between MLW-6 and MLW-4 separates a zone of groundwater inflow to the lake at MLW-6 ($\delta^{18}O$ = −3.35‰ and δ^2H = −15.5‰) from a zone of groundwater outflow at MLW-4 ($\delta^{18}O$ = +0.95‰ and δ^2H = +2.5‰). This finding demonstrates that patterns of lake water leakage to the groundwater system can be quite complex. Even though there is no direct evidence of transient behavior, stable isotope

patterns indicate that the spatial variability in lake water leakage could be related to transient water table behavior.

The use of stable isotopes can provide insights into the interaction between groundwater and lakes that steady state groundwater flow modeling or synoptic head measurements cannot. Discrepancies between monthly groundwater flow derived from detailed hydrologic budget calculations and simulated net groundwater flow for Lake Barco were attributed to the formation of highly transient mounds occurring in the water table close to the lake [Lee, 1995]. The formation of transient water table mounds has been detected in a study of a seepage lake similar to Lake Barco, but located farther south in the Central Lake physiographic division of Florida [Lee et al., 1991; Lee and Swancar, 1995] and in a kettle hole lake [Cherkauer and Zager, 1989].

Influence of lake water leakage. The isotopic compositions of groundwater downgradient from Lake Barco (MLW-4 and 2PNB well nest) have enriched values relative to meteoric water and plot along a mixing line of slope 4.76 between the isotopic composition of evaporated Lake Barco water and groundwater upgradient of the lake (Figure 6). *Stichler and Moser* [1979] describe a similar pattern for mixing (along a slope of 6) between evaporated lake water and groundwater in the upper Rhine Valley of Germany. The isotopic shift in the composition of groundwater downgradient from Lake Barco provides evidence for lateral flow from the lake toward the downgradient sites, despite the strong vertically downward head gradient at the nested wells at the 2PNB site. The isotopic composition of groundwater downgradient from Lake Barco was nearly identical for samples collected during the three separate occasions (Table 2), and for the sake of clarity, only the isotopic compositions for the most recent samples (August and September 1992) are shown in Figure 6.

The mixing line between evaporated Lake Barco water and meteoric groundwater is described by the expression $\delta^2H\%o = 4.76\delta^{18}O\%o - 0.41$ ($r^2 = 0.992$). The relative position of the sites downgradient from Lake Barco along this line, representing a two end-member mixing model, indicates the relative proportion of lake water outflow or leakage that has mixed with meteoric water (recharge water). Isotope mass balance indicates that the largest fraction of lake water leakage (67%) occurred in water samples from well MLW-4 (which is located directly beneath the lake) and 2PNB-FL (63%), which is hydraulically connected to the lake as a result of the breached confining unit. Progressively smaller amounts of lake water leakage have mixed with groundwater from 2PNB-80 to 2PNB-20 (47 to 11%).

Distinct differences in the isotopic composition of lake water, rainfall, and groundwater allowed for a greater precision for detecting the mixing proportion of lake water in groundwater. The sensitivity of the method for detecting lake water in groundwater can be determined by the following expression [Payne, 1983]:

$$S = \pm X/Y, \tag{2}$$

where $\pm X$ is the variability (1σ) of the isotopic composition of the lake, in per mil; and Y is the difference between the isotopic composition of lake water and groundwater, in per mil. Using this expression, the calculated limit of detection of lake water in groundwater is 4.3% using data for both $\delta^{18}O$ and δ^2H. This high-precision estimate provided a high degree of confidence for using mixing ratios of lake water leakage and meteoric (recharge) water to model the chemical evolution of
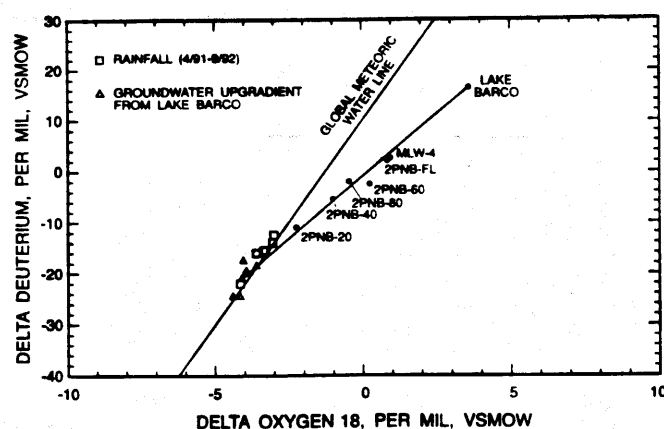

Figure 6. Deuterium and oxygen 18 content of rainfall, groundwater, and lake water, September, 1992, compared to the global meteoric water line (MWL).

groundwater downgradient from Lake Barco that is discussed in paper 2 [Katz et al., this issue].

Lake water becomes anoxic as it passes through the organic-rich sediments at the bottom of the lake (Figure 2), and as a result of microbial processes in the organic-rich sediments and in sediment beneath the lake, the lake water leakage has elevated concentrations of dissolved hydrogen sulfide and methane (Table 3). The presence of reduced species provides further evidence for the leakage of lake water into groundwater. There is a direct correlation between methane concentration and the proportion of lake water leakage. The highest methane concentrations were observed in water from MLW-4 and 2PNB-FL, the two waters which have the highest proportion of lake water leakage, and the lowest methane concentration was measured in water from 2PNB-20, which has the smallest proportion of lake water leakage. However, because the methane concentrations do not vary linearly with mixing fraction (Figure 7), methane concentrations are not conservative, and additional sources for the production of methane probably occur in the groundwater beneath Lake Barco [see Katz et al., this issue].

Age of Groundwater

CFCs were used to determine the age of groundwater near Lake Barco. The age of groundwater refers to the time since the recharge water became isolated from the unsaturated zone atmosphere and is determined as the difference between the CFC-modeled recharge date and the year 1992.

CFC-Modeled Recharge Dates

The concentration of a particular CFC compound in groundwater is dependent on the equilibrium partitioning between rainwater and the partial pressures of the particular CFC compound at the base of the unsaturated zone. A recharge temperature of 21°C was used to calculate the partitioning of CFCs between water and the unsaturated zone atmosphere based on three independent measurements: (1) the mean annual air temperature of 21°C measured at Gainesville, Florida, for the period 1961–1990 [Owenby and Ezell, 1992]; (2) the mean groundwater temperature was 23 ± 2°C, measured during sampling in 1991–1992; and (3) a groundwater temperature of 19 ± 2.5°C was calculated based on measurements of

Table 3. Concentration of Dissolved Gases in Groundwater

| Well Name	Date of Sample	Water Temperature, °C	N_2	O_2	Ar	CO_2	H_2S	CH_4
1PNB-20	Sept. 1, 1992	25.	0.568	0.218	0.0148	0.286	0.0	0.0
1PNB-40	Aug. 31, 1992	25.	0.565	0.177	0.0135	0.385	0.0	0.0
1PNB-60	Aug. 31, 1992	26.	0.632	0.208	0.0152	0.362	0.0	0.0
1PNB-FL	May 11, 1991	22.5	0.569	0.200	0.0139	0.011	0.0	0.0
1PNB-FL	Aug. 31, 1992	23.	0.573	0.194	0.0141	0.049	0.0	0.0
2PNB-20	Sept. 2, 1992	22.	0.668	0.001	0.0160	1.31	0.005	0.0344
2PNB-40	Sept. 2, 1992	23.	0.654	0.001	0.0154	1.41	0.004	0.0627
2PNB-60	Sept. 2, 1992	23.	0.655	0.000	0.0155	1.86	0.001	0.0639
2PNB-80	Sept. 1, 1992	23.	0.685	0.000	0.0162	1.10	0.010	0.0428
2PNB-FL	May 12, 1991	22.5	0.783	0.004	0.0176	0.240	0.001	0.212
2PNB-FL	Sept. 1, 1992	23.	0.731	0.000	0.0166	0.274	0.001	0.156
MLW-4	Sept. 3, 1992	24.	0.700	0.000	0.0169	1.66	0.002	0.695

Values are in millimoles per liter.

dissolved argon and nitrogen concentrations in water samples (collected from 10 wells during May 1991 and August and September 1992; Table 3) and their equilibrium solubilities (Figure 8) from Henry's law [Weiss, 1970]. The production of N_2 from microbial reduction of nitrate is unlikely in this system because the concentration of nitrate is near the analytical detection limit (0.02 mg/L) in aerobic groundwater upgradient from Lake Barco. An uncertainty in the recharge temperature of $\pm 2°C$ would result in an uncertainty in the groundwater age of ± 2 years for waters recharged in 1978 and later and ± 1 year for groundwater recharged prior to 1978.

During August and September 1992, water was collected from nine wells in the 1PNB and 2PNB nests, from three in-lake wells, and at two depths below the surface of Lake Barco. These water samples were analyzed for CFC-11, CFC-12, and CFC-113, and these data are presented in Table 4. Means and standard deviations for CFC-modeled recharge dates for each of the three compounds are shown in Figure 9 for different depths in the groundwater system and in the lake. Groundwater becomes progressively older along the vertical flow path at the 1PNB site, from a date of 1989 about 1 m below the water table to a date of 1978 at the top of the UFA, about 27 m below the water table. Groundwater from sites upgradient from Lake Barco has mean CFC-11, CFC-12, and CFC-113 modeled recharge dates that generally agree within 1

year, with the exception of water from the 1PNB-FL well. At this depth, CFC-113 modeled recharge dates are younger than those obtained using measurements of CFC-11 and CFC-12 concentrations and could represent some contamination of the sample with CFC-113. CFC-12 modeled dates for these waters closely match the CFC-12 modeled recharge dates obtained from samples collected in May 1991 [Katz, 1993]. MLW-2, which receives water from upgradient near 1PNB-20, is slightly older (1985 $\pm$ 1.2) than water collected from 1PNB-20 (1987.4 $\pm$ 1.2). The CFC-12 modeled recharge date for groundwater at the MLW-6 site (Figure 9) is 1989 $\pm$ 0.8. On the basis of its stable isotopic composition, this location is receiving recharge directly from rainfall. The relatively young age of this water suggests that it is flowing into Lake Barco and this location (MLW-6) is not receiving any outflow of water from the lake. This finding is consistent with the aforementioned stable isotopic data and the influence of transient water table mounding.

Lake water was expected to be in equilibrium with atmospheric levels of CFCs because the lake is aerated and well mixed and receives about 10% of its hydrologic income from upgradient groundwater [Lee, 1995]. The CFC-12 modeled recharge date for the 3-m depth was 1990 $\pm$ 1.9, which essentially represents present-day recharge. However, the CFC-12 modeled recharge date was 1988 $\pm$ 0.2 for shallow lake water (1 m depth), which is surprising given the opportunity for exchange between shallow lake water and the atmosphere. The removal of CFCs from the shallow lake water could be related to the affinity of these compounds to sorb to particulate organic carbon that eventually settles to the bottom of the lake
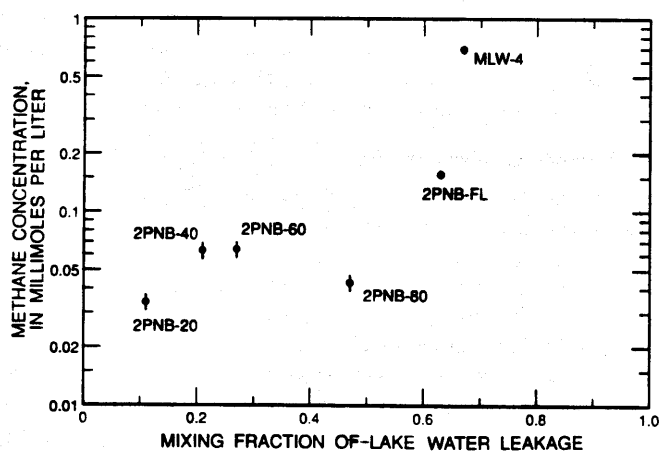
Figure 7. Methane concentration in groundwater as a function of the mixing proportion of lake water leakage and groundwater.
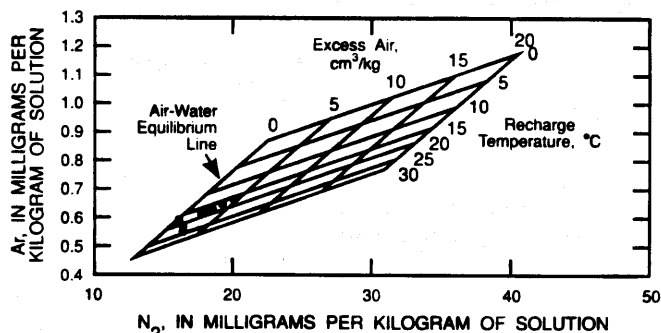
Figure 8. Dissolved nitrogen and argon gas compositions of groundwater near Lake Barco.

Table 4. Summary Data for CFC-11, CFC-12, and CFC-113 in Groundwater and Lake Water, August and September 1992

Sample Number	Time	Concentration in Solution, pg/kg			Calculated Atmospheric Partial Pressure, pptv			Model Dates		
		CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
Sample 1PNB-20, September 1, 1992										
1	0920	378.3	182.2	28.0	223.4	444.3	42.6	1985.5	1987.5	1984.5
2	0925	418.7	212.4	37.8	247.3	518.1	57.5	1992.7	1992.5	1987.0
3	0930	373.8	185.2	27.7	220.8	451.7	42.2	1985.5	1987.5	1984.5
4	1015	400.7	201.6	37.5	236.6	491.6	57.0	1987.0	1990.5	1986.5
5	1025	391.4	188.6	26.9	231.2	459.9	41.0	1986.5	1988.0	1986.0
6	1038	399.9	201.5	36.9	236.2	491.5	56.1	1987.0	1990.0	1984.5
No.								6	6	6
Mean								1987.36	1989.33	1985.58
s.d.								2.45	1.84	1.10
Sample 1PNB-40, August 31, 1992										
1	1705	2058.1	146.1	68.6	1215.6	356.4	104.5	C	1983.0	C
2	1722	1802.1	161.9	26.9	1064.4	394.9	40.9	C	1985.0	1984.5
3	1730	2162.4	143.6	19.4	1277.2	350.2	29.5	C	1982.5	1981.5
4	1820	1887.6	157.0	27.0	1114.8	382.9	41.0	C	1984.5	1984.5
5	1825	2547.9	150.4	55.6	1504.8	366.8	84.6	C	1983.6	1992.5
6	1830	1765.6	50.3	29.3	1042.8	122.7	44.6	C	1969.5	1985.0
No.								C	5	5
Mean								C	1983.70	1985.60
s.d.									0.93	3.67
Sample 1PNB-60, August 31, 1992										
1	1447	336.1	121.3	23.9	198.5	295.7	36.3	1983.0	1979.0	1983.0
3	1500	294.7	111.5	19.5	174.1	272.0	29.7	1980.5	1977.5	1981.5
4	1504	307.3	124.1	18.0	181.5	302.6	27.4	1981.5	1979.5	1981.0
5	1545	309.8	117.1	19.4	183.0	285.5	29.5	1981.5	1978.0	1981.5
6	1556	311.4	128.2	19.7	183.9	312.8	30.0	1981.5	1977.5	1981.5
7	1601	291.4	111.9	16.0	172.1	272.9	24.4	1980.0	1976.5	1980.0
No.								6	6	6
Mean								1981.33	1978.67	1981.50
s.d.								0.94	1.11	1.04
Sample 1PNB-FL, August 31, 1992										
5	1225	269.8	119.0	22.8	159.4	290.2	34.8	1978.5	1978.5	1983.0
6	1230	259.5	123.9	18.9	153.3	302.2	28.8	1978.0	1979.5	1981.0
7		236.9	105.4	16.2	139.9	257.1	24.6	1976.5	1976.5	1980.0
8	1325	264.1	126.3	22.2	156.0	308.1	33.8	1978.0	1980.0	1982.5
9	1335	242.6	109.1	23.1	143.3	266.1	35.1	1977.0	1977.0	1983.0
No.								5	5	5
Mean								1977.60	1978.30	1981.90
s.d.								0.73	1.36	1.20
Sample 2PNB-20, September 2, 1992										
1	1205	65.1	78.3	30.3	38.5	191.1	46.2	1967.0	1973.5	1985.0
2	1215	40.9	66.7	16.9	24.2	162.7	25.7	1964.5	1972.0	1980.5
3	1225	49.1	61.2	21.9	29.0	149.3	33.3	1965.5	1971.0	1982.5
4	1322	113.8	119.6	19.8	67.2	291.7	30.2	1970.5	1978.5	1981.5
5	1325	63.1	85.6	20.0	37.3	208.7	30.4	1967.0	1974.0	1981.5
6	1330	104.1	74.5	13.5	61.5	181.7	20.5	1970.0	1973.0	1978.0
No.								6	6	1
Mean								1967.42	1973.67	1978.0
s.d.								2.19	2.37	...
Sample 2PNB-40, September 2, 1992										
1	940	21.6	49.9	9.4	12.8	121.8	14.4	1961.0	1969.5	1974.0
2	950	89.1	52.0	0.0	52.6	126.9	0.0	1969.0	1969.5	1966.0
3	955	13.3	42.1	0.0	7.9	102.6	0.0	1958.0	1968.0	1966.0
4	1055	0.0	52.1	0.0	0.0	127.1	0.0	1945.0	1969.5	1966.0
5	1100	7.5	45.1	0.0	4.4	110.0	0.0	1955.5	1968.5	1966.0
6	1105	0.0	58.8	0.0	0.0	143.4	0.0	1945.0	1971.0	1966.0
No.								3	6	5
Mean								1962.67	1969.33	<1966
s.d.								4.64	0.94	...
Sample 2PNB-60, September 2, 1992										
1	1500	2.1	52.8	0.0	1.3	128.8	0.0	1951.5	1970.0	1966.0
2	1505	28.3	87.5	0.0	16.7	213.5	0.0	1962.5	1974.5	1966.0
3	1510	17.0	58.7	5.1	10.0	143.3	7.8	1959.5	1971.0	1970.5
4	1555	33.1	87.6	0.0	19.5	213.6	0.0	1963.0	1974.5	1966.0
5	1600	14.1	60.7	7.5	8.3	147.9	11.4	1958.5	1971.0	1972.5
6	1605	61.6	63.4	0.0	36.4	154.6	0.0	1966.5	1971.5	1966.0
No.								5	6	4
Mean								1962.00	1972.08	<1966
s.d.								2.83	1.77	...

Table 4. (continued)

Sample Number	Time	Concentration in Solution, pg/kg			Calculated Atmospheric Partial Pressure, pptv			Model Dates		
		CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
				Sample 2PNB-80, September 1, 1992						
1	1644	14.7	61.0	0.0	8.7	148.8	0.0	1958.5	1971.0	1966.0
3	1656	22.0	64.1	0.0	13.0	156.2	0.0	1961.0	1971.5	1966.0
4	1737	10.4	72.2	0.0	6.1	176.1	0.0	1956.5	1972.5	1966.0
5	1750	19.0	66.3	0.0	11.2	161.7	0.0	1960.0	1972.0	1966.0
6	1757	17.7	69.5	0.0	10.5	169.5	0.0	1960.0	1972.5	1966.0
No.								5	5	5
Mean								1959.20	1971.90	<1966
s.d.								1.57	0.58	...
				Sample 2PNB-FL, September 1, 1992						
2	1308	4.9	9.0	0.0	2.9	21.9	0.0	1954.0	1956.5	1966.0
3	1318	13.1	14.6	0.0	7.7	35.5	0.0	1958.0	1960.0	1966.0
4	1327	7.7	8.0	0.0	4.5	19.6	0.0	1955.5	1956.0	1966.0
5	1404	13.4	7.4	0.0	7.9	18.1	0.0	1958.0	1955.5	1966.0
6	1409	22.2	11.6	0.0	13.1	28.3	0.0	1961.0	1958.5	1966.0
7	1413	18.4	8.3	0.0	10.9	20.3	0.0	1960.0	1956.0	1966.0
No.								6	6	6
Mean								1957.75	1957.08	<1966
s.d.								2.41	1.62	...
				Sample L.BARCO 1 m, August 31, 1992						
1	1745	282.4	142.3	22.9	229.3	460.9	50.7	1986.0	1988.0	1985.5
2	1745	295.1	140.3	24.0	239.6	454.2	53.0	1987.0	1988.0	1986.0
3	1745	288.5	139.3	23.9	234.2	451.0	53.0	1986.5	1987.5	1986.0
No.								3	3	3
Mean								1986.50	1987.83	1987.83
s.d.								0.41	0.24	0.24
				Sample L.BARCO 3 m, September 3, 1992						
1	1735	277.4	144.9	29.0	225.2	469.1	64.2	1986.0	1989.0	1988.0
2	1740	299.8	157.8	27.8	243.4	511.1	61.6	1987.5	1992.0	1987.5
3	1745	278.1	144.6	29.0	225.8	468.3	64.1	1986.0	1988.5	1988.0
4	1750	301.2	161.0	32.0	244.5	521.3	70.9	1987.5	1993.0	1989.0
5	1755	274.3	142.7	28.2	222.7	462.0	62.5	1985.5	1988.5	1987.5
No.								5	5	5
Mean								1986.50	1990.20	1988.00
s.d.								0.84	1.91	0.55
				Sample MLW-2, September 3, 1992						
1	1102	381.1	168.1	30.5	225.1	409.9	46.5	1986.0	1986.0	1985.0
2	1107	409.4	195.9	35.4	241.8	477.7	53.9	1987.0	1989.5	1986.0
3	1112	392.3	183.4	30.7	231.7	447.4	46.8	1986.5	1987.5	1985.0
4	1117	406.0	195.3	34.6	239.8	476.4	52.7	1987.0	1989.5	1986.0
5	1127	367.9	174.9	29.6	217.3	426.6	45.1	1985.0	1987.0	1985.0
No.								5	5	5
Mean								1986.30	1987.90	1985.40
s.d.								0.75	1.39	0.49

C denotes contaminated sample; pptv denotes parts per trillion volume; model dates denote CFC-modeled recharge date; no. denotes number of samples analyzed; and s.d. denotes standard deviation; three dots denotes not calculated. Barometric pressure for all samples was 760 mm of mercury. Recharge temperature for groundwater and lake water samples was 21°C and 29°C, respectively.

[*Imboden and Schwarzenbach*, 1985]. Other in-lake processes could account for removal of CFCs in the shallower part of the lake including photolysis and gas exchange due to slightly higher water temperatures near the surface of the lake.
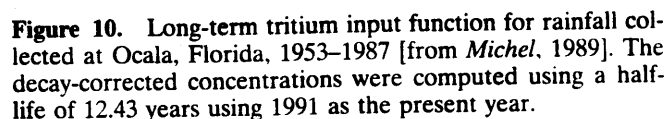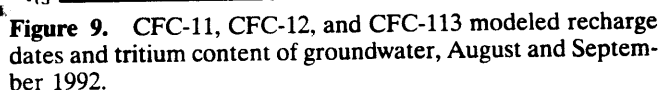
Downgradient from Lake Barco at the 2PNB site, groundwater also becomes progressively older with depth below the water table, from a date of 1974 about 1 m below the water table to a date of 1957 at the top of the UFA, about 25 m below the water table (Figure 9). In contrast to the agreement between CFC-11 and CFC-12 modeled dates at sites upgradient from the lake, CFC-11 modeled recharge dates were about 6 to 12 years earlier (older) than CFC-12 modeled recharge dates for groundwater from all depths at the 2PNB nest with the

exception of the 2PNB-FL well. The loss of CFC-11 from reducing groundwater is most likely related to higher rates of microbial degradation of CFC-11 relative to CFC-12 [*Semprini et al.*, 1990; *Lovley and Woodward*, 1992].

Water from MLW-4 and 2PNB-FL had the highest methane concentrations of 5.9 and 1.4 mg/L, respectively; however, the CFC-11 modeled recharge dates for water from MLW-4 and 2PNB-FL closely match the CFC-12 modeled recharge dates, within ±2 years. This could indicate that in groundwater where extensive methanogenesis is occurring, both CFC-11 and CFC-12 are being degraded. CFC-11 has a higher aqueous solubility than CFC-12, so relatively more of its mass is removed from solution than CFC-12. *Lovley and Woodward*

[1992] reported that CFC-11 uptake was consistently faster than CFC-12 uptake in anaerobic soils and sediments. Their results indicated that CFC-11 uptake was caused by nonenzymatic as well as enzymatic processes. Based on these observed losses of CFCs in anaerobic waters, caution needs to be applied when using these compounds as dating tools or as hydrologic tracers in anaerobic environments. Other environmental tracers, such as ^3H, $^3H/^3He$ [Schlosser et al., 1989; Solomon and Sudicky, 1991], and ^{85}Kr [Smethie et al., 1992] are needed to assess the validity of CFC-modeled recharge dates in groundwater under anaerobic conditions.

Comparison of CFC-Modeled Recharge Dates to Tritium Data

The CFC recharge dates for groundwater were compared with long-term ^3H concentrations in rainfall. The long-term ^3H input function for the study area (Figure 10) was derived from Michel's [1989] data for the 1953–1983 period for the IAEA precipitation monitoring station in Ocala, Florida, located approximately 51 km south of Lake Barco. Annual volume-weighted mean concentrations of ^3H for 1984–1987 were calculated from measurements of rainfall (monthly composite samples) at the Ocala station. The decay-corrected concentrations (Figure 10) were based on the 1991 sampling year and a ^3H half-life of 12.43 years.

The annual input concentration of ^3H (corrected for decay) is assumed to be accurately represented by the annual volume-weighted mean concentration. This assumption is based on the finding that recharge to groundwater in the Lake Barco catchment occurs mainly during the winter and summer rainy seasons and when rainfall exceeds evapotranspiration. During the period April 1989 to December 1990, rainfall exceeded evaporation in September and December 1989, and in February, June, and October 1990 [Lee, 1995]. Based on a 30-year period (1961–1990) of rainfall and evaporation measurements at the National Weather Service station in Gainesville, Florida, located approximately 30 km west of the study area, the monthly mean rainfall exceeded the monthly mean evaporation for December, January, February, August, and September.

Figure 10. Long-term tritium input function for rainfall collected at Ocala, Florida, 1953–1987 [from Michel, 1989]. The decay-corrected concentrations were computed using a half-life of 12.43 years using 1991 as the present year.

All groundwater and lake water samples had ^3H concentrations that represent post-1953 recharge (Figure 9). Tritium concentrations in most samples of groundwater were less than 11 TU. Waters that originated from rainfall prior to nuclear bomb testing would have maximum ^3H concentrations of 0.2–0.8 TU by the early 1990s, assuming estimates given by Thatcher [1962] of 2–8 TU [Plummer et al., 1993]. The ^3H concentration in samples of groundwater and lake water was nearly identical for the three separate occasions (Table 5) and generally agreed within $\pm 1\sigma$. The highest ^3H concentrations were measured in water from 2PNB-FL (18.6 and 20.7 TU), and these concentrations could represent recharge related to the late 1950s to mid 1960s bomb pulse or a mixture of recharge from the mid 1960s with more recent water.

Tritium concentrations in groundwater can be affected by hydrodynamic dispersion, particularly for waters recharged prior to 1964. Dispersion can have a greater effect on ^3H dating than on CFC dating of groundwaters [Plummer et al., 1993]. Concentrations of ^3H in groundwater at the 2PNB-FL site (18.7 and 20. TU) could represent bomb pulse concentrations, and waters recharged during 1964–1965 have been shown to be little affected by dispersion [Plummer et al., 1993]. No attempt was made in this study to adjust ^3H concentrations in groundwater that received recharge prior to 1964 and after 1965. Hydrodynamic dispersion was not an important process in modifying the concentration of ^3H or CFCs in shallow groundwater (30 m) flow systems on the Delmarva Peninsula, in the mid-Atlantic coastal plain [Dunkle et al., 1993; Reilly et al., 1994].

The ^3H concentrations measured in samples of groundwater and lake water also were similar to the ^3H concentrations measured in monthly samples of rainfall collected during October 1991 to September 1992 (Figure 11). The high concentration in rainfall during May 1992 (26.4 TU) was probably caused by the seasonal breakup of the tropopause between 30° and 60°N which occurs during the spring each year [Michel, 1989] when water vapor with elevated concentrations of ^3H is released from the stratosphere into the troposphere.

The concentrations of ^3H measured in water samples from the sites downgradient from Lake Barco could only represent recharge of water prior to 1991. Mass balance calculations

Figure 9. CFC-11, CFC-12, and CFC-113 modeled recharge dates and tritium content of groundwater, August and September 1992.

Table 5. Tritium Content of Groundwater, Lake Water, and Rainfall, May 1991 to September 1992.

Site Name	Date of Sample	Tritium, TU	$\pm 1\sigma$
1PNB-20	May 10, 1991	5.4	0.4
	Oct. 9, 1991	3.7	0.5
	Sept. 1, 1992	5.3	0.4
1PNB-40	May 10, 1991	7.2	0.4
	Oct. 9, 1991	5.5	0.5
	Aug. 31, 1992	4.9	0.5
1PNB-60	May 11, 1991	8.6	0.5
	Oct. 9, 1991	7.8	0.5
	Aug. 31, 1992	6.4	0.4
1PNB-80	Oct. 10, 1991	7.0	0.8
1PNB-FL	May 11, 1991	7.2	0.5
	Oct. 9, 1991	5.8	0.5
	Aug. 31, 1992	6.4	0.4
2PNB-20	May 11, 1991	6.6	0.4
	Oct. 9, 1991	6.3	0.4
	Sept. 2, 1992	6.0	0.3
2PNB-40	May 12, 1991	9.1	0.5
	Oct. 9, 1991	8.8	0.6
	Sept. 2, 1992	6.9	0.4
2PNB-60	Oct. 9, 1991	5.9	0.5
	Sept. 2, 1992	6.6	0.4
2PNB-80	May 12, 1991	10.8	0.5
	Oct. 9, 1991	9.9	0.6
	Sept. 1, 1992	10.3	0.5
2PNB-FL	May 12, 1991	20.7	0.7
	Oct. 9, 1991	18.6	1.0
	Sept. 1, 1992	18.7	0.7
MLW-2	May 11, 1991	6.1	0.4
	Oct. 9, 1991	6.7	0.4
	Sept. 3, 1992	5.2	0.5
MLW-4	May 11, 1991	6.5	0.4
	Oct. 10, 1991	5.9	0.4
	Sept. 3, 1992	5.8	0.4
MLW-6	May 11, 1991	3.7	0.4
	Oct. 9, 1991	3.7	0.3
	Sept. 4, 1992	5.0	0.4
Rainfall	Oct. 8 to Nov. 26, 1991	7.7	1.2
	Dec. 31, 1991 to Jan. 28, 1992	1.3	1.0
	Jan. 28 to Feb. 25, 1992	5.5	1.0
	Feb. 25 to March 31, 1992	3.7	1.0
	March 31 to April 28, 1992	3.2	1.2
	April 28 to May 26, 1992	26.4	1.8
	May 26 to June 30, 1992	2.6	1.1
	June 30 to July 28, 1992	4.2	1.1
	July 28 to Aug. 15, 1992	1.6	1.3
	Aug. 15 to Sept. 28, 1992	3.7	1.2
Lake Barco	May 11, 1991	6.3	0.4
	Oct. 10, 1991	4.7	0.4
	Sept. 3, 1992	5.7	0.4
WTB-1	Oct. 9, 1991	4.2	0.4
WTB-5	Oct. 9, 1991	6.9	0.4
WTB-14	Oct. 9, 1991	6.8	0.4
WTB-20	May 11, 1991	6.4	0.4
3PNB-20	Oct. 10, 1991	4.8	0.4
	Oct. 10, 1991	6.6	0.5

TU denotes tritium units; σ denotes analytical standard deviation.

indicate that at present (1992) ^3H concentrations in rainfall and lake water cannot account for the observed ^3H concentrations and the mass transfer at each of these sites. If mixing proportions of meteoric water and lake water leakage have remained constant during the past 40 years to produce the observed stable isotopic composition of groundwater, then older waters with corresponding higher ^3H concentrations can only account for their observed ^3H content.

The difficulty of age dating shallow groundwater is demonstrated by some of the limitations encountered using the ^3H

and CFC methods. The ^3H age-dating method in the southeastern United States is limited by (1) declining ^3H concentrations in groundwater, (2) the passing of the ^3H transient (or peak concentration) through shallow groundwater, and (3) the complex input function, which is subject to seasonal perturbations caused by variations in types of storms, and atmospheric mixing. Furthermore, the transients in ^3H input are significantly affected by hydrodynamic dispersion [*Solomon and Sudicky*, 1991]. In contrast, the limitations encountered in using the CFC age-dating technique for shallow groundwater are related to alteration of the concentration of CFC compounds by local contamination sources and biological processes that remove CFCs (especially CFC-11) in anaerobic sediments [*Lovley and Woodward*, 1992] rather than by hydrodynamic dispersion, because of the smooth continually increasing input function for CFCs (CCl_3F, CCl_2F_2, and $C_2Cl_3F_3$) [*Plummer et al.*, 1993]. This method is also more sensitive to contamination during sampling.

Comparison of CFC-Modeled Recharge Dates With Hydraulic Analyses

Rates of groundwater flow estimated from CFCs and ^3H were compared with hydraulic analyses using numerical simulation techniques. These two techniques have been used together to examine the interaction of groundwater and stream water and in combination have provided useful hydraulic information on aquifer properties, solute transport processes, and distribution and rates of recharge [*Reilly et al.*, 1994]. Transient simulations with a three-dimensional (3-D) ground-
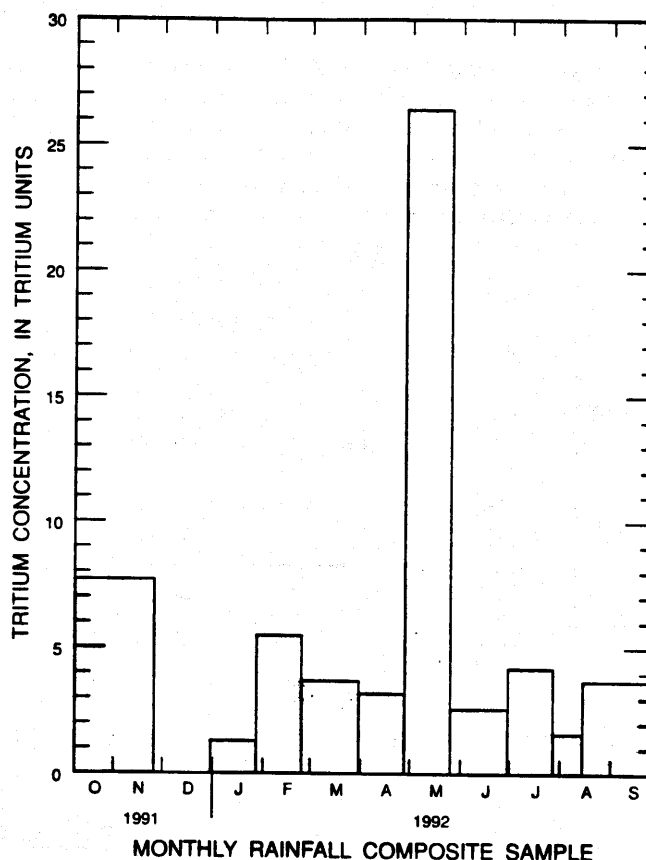
Figure 11. Monthly variation of tritium concentrations in rainfall collected at Lake Barco, October 1991 through September 1992.

water flow model were used to predict monthly groundwater fluxes to Lake Barco during January 1989 to December 1990, a period characterized by below average rainfall and above average evaporation. The areal and vertical discretization of the variably spaced model grid, boundary conditions, hydraulic properties for the lake and groundwater flow system, calibration procedures, and the effect of transient water table mounds are described in detail by *Lee* [1995]. Results from the 3-D flow model, which simulated steady state flow in the surficial and intermediate confining unit surrounding the lake, were used in a particle-tracking program (MODPATH) [*Pollock*, 1989]. Path lines and average travel times for groundwater flow in the basin were simulated with MODPATH using average annual recharge to the lake and groundwater basin and long-term average lake stage and head values for the UFA [*Lee*, 1995].

The travel times determined from CFC-modeled recharge dates and ^{3}H were consistent with those obtained using the particle-tracking program. The CFC-12 modeled recharge dates reflect a travel time to the UFA of about 14 years (12–15 years based on uncertainty in CFC-12 modeled recharge ages) near site 1PNB and a longer travel time of approximately 25–35 years near site 2PNB. Travel times predicted by the particle-tracking program were around 6–11 years near site 1PNB, whereas those near site 2PNB were about 15–22 years. The shorter travel times predicted by the particle-tracking program could reflect higher modeled hydraulic conductivities than those estimated using CFC-modeled recharge dates.

Flow velocities obtained from CFC-12 modeled recharge dates were used to estimate vertical hydraulic conductivity ($K_{v(calc)}$) for the sediments that compose the surficial aquifer and the intermediate confining unit at the 1PNB site, and for the lake sediments. Values of $K_{v(calc)}$ were compared with vertical hydraulic conductivities used in the numerical simulation of groundwater flow. $K_{v(calc)}$, in meters per day, was computed based on the Darcy equation in the form

$$K_{v(calc)} = v_{ave} n/(\Delta h/\Delta L) \qquad (3)$$

where $K_{v(calc)}$ is the vertical hydraulic conductivity, in meters per day; v_{ave} is the average linear flow velocity (distance traveled divided by the age of water in days); n is the porosity; Δh is the change in hydraulic head, in meters; and ΔL is the length of the flow path, in meters. Substituting L/t for v_{ave} in (3) yields the following expression for $K_{v(calc)}$:

$$K_{v(calc)} = \Delta L^2 n/\Delta t \Delta h \qquad (4)$$

where Δt is the age of the water in days. The age of groundwater at the 1PNB sites was obtained by subtracting the CFC-12 modeled recharge date from 1992 (the year of sample collection) and converting this value in years to days.

At the 1PNB site, $K_{v(calc)}$ was 0.17 and 0.033 m/d for the surficial and intermediate confining unit, respectively. $K_{v(calc)}$ ranged from 0.08 to 0.28 m/d for the surficial aquifer using porosity values of 0.25 to 0.40 [*Fetter*, 1988] and incorporating the uncertainty in the CFC-12 modeled recharge date. For the intermediate confining unit, $K_{v(calc)}$ ranged from 0.016 to 0.048 m/d using the aforementioned range in porosity values and CFC-12 modeled recharge dates. Values of K_v that were used in the groundwater flow model were 0.6 and 0.09 m/d for the surficial aquifer and the intermediate confining unit, respectively. K_v for the surficial aquifer was obtained by dividing the horizontal hydraulic conductivity calculated from slug tests ($K_h = 6.0$ m/d) by 10, the estimated anisotropy of the surficial

aquifer [*Lee and Swancar*, 1995]. A reasonable model calibration was obtained using this K_v for the surficial aquifer and a K_v of 0.09 m/d for the intermediate confining unit. A porosity of 0.25 was assumed for both the surficial aquifer and the intermediate confining unit in the groundwater flow model.

A major uncertainty in estimating travel times downgradient from Lake Barco is an accurate determination of the hydraulic conductivity of the low-permeability lake sediments. Results from the transient 3-D groundwater flow model [*Lee*, 1995] indicated a much steeper vertical head drop directly beneath the lake instead of the evenly distributed head drop between the lake bed and the UFA (Figure 5). A significant part of the modeled head drop occurred across the low-conductivity lake sediments. A reasonable calibration of the flow model was obtained by assuming that the hydraulic conductivity of the lake sediments was 2–5% of the K_v in the adjacent surficial aquifer cells (0.09 m/d). Unfortunately, the in-lake wells could not be used to provide reliable head measurements, and therefore direct estimates of the vertical leakage rates could not be made. K_v was calculated for the lake sediments using the CFC-12 age of water at MLW-4 and (4). For this calculation it was assumed that it would take lake water leakage 33.3 years to move through the 3 m of organic-rich sediments at the bottom of the lake and 0.7 year to move through 1 m of surficial material below the lake sediments (based on rates of groundwater flow in the surficial aquifer from 1PNB-20 to 1PNB-40). These travel times resulted in a $K_{v(calc)}$ for the lake sediments of 0.019 m/d, with a range of 0.011–0.023. The $K_{v(calc)}$ of lake sediments is approximately an order of magnitude less than the $K_{v(calc)}$ for the intermediate confining unit and about an order of magnitude greater than values used in the groundwater flow model (0.0018–0.0045 m/d).

The consistency of K_v values between the two sources of data indicates that CFC-modeled recharge dates can be used in conjunction with other aquifer properties such as porosity and hydraulic head data to calculate the vertical or horizontal conductivity of shallow aquifers and confining units. Uncertainties in hydraulic head change, porosity, and age of water can introduce sources of error in calculating the hydraulic conductivity values. Small errors in Δh (which in some cases were near the limit of measurement of 3 mm) could introduce relatively large uncertainties in K_v or K_h; however, it is likely that errors in any of the parameters in (4) are less than a factor of 2. Therefore, for a worst case scenario, the uncertainty in $K_{v(calc)}$ would be approximately 1 order of magnitude. This uncertainty is similar to the differences between $K_{v(calc)}$ and K_v values used in the groundwater flow model.

Summary and Conclusions

The hydrochemical interaction between groundwater and lake water leakage is enhanced by the presence of highly conductive sediments that fill solution features in underlying limestone. A direct conduit is provided for recharge of anaerobic water to the Upper Floridan aquifer. The combined use of stable isotopes (^{18}O and ^{2}H) and CFCs have provided an effective means of quantitatively determining complex groundwater flow patterns and flow rates in a mantled karst lake basin.

The stable isotopic composition (δ^{18}O and δ^2H) of rainfall and groundwater upgradient from Lake Barco (sampled near the water table and at several depth below it) plot in close proximity along the global meteoric water line. In contrast, the

$\delta^{18}O$ and δ^2H composition of lake water and groundwater downgradient from the lake was enriched relative to meteoric water as a result of evaporation and mixing. The relation between δ^2H and $\delta^{18}O$ in groundwater downgradient from the lake can be described by the expression δ^2H (per mil) $= 4.76\delta^{18}O$ (per mil) -0.41 ($r^2 = 0.992$). These distinct differences among the stable isotopic composition ($\delta^{18}O$ and δ^2H) of lake water, rainfall, and groundwater contributed to the effectiveness of the development of a mixing model that accounted for the enriched isotopic composition of groundwater downgradient from the lake. The model indicated that the amount of lake water leakage that mixed with infiltrating meteoric water ranged from 11 to 67%, with a limit of detection of lake water in groundwater of 4.3% (confirmed independently by using data for both $\delta^{18}O$ and δ^2H). This high-precision estimate provided a high degree of confidence for using these mixing ratios of lake water leakage and meteoric (recharge) water to model the chemical evolution of groundwater downgradient from Lake Barco. Stable isotope patterns also indicated evidence of transient water table mounding near the lake, even though there was no direct evidence of this behavior. The use of stable isotopes can provide insights into the interaction between groundwater and lakes that steady state groundwater flow modeling or synoptic head measurements cannot.

The transient environmental tracers, CFCs and ^3H, provided valuable information on the age of recharge water in this hydrologically complex groundwater-lake system. CFC-modeled recharge dates were consistent with recharge dates estimated from observed ^3H data. Upgradient from Lake Barco where the direction of groundwater flow is downward, the dates for groundwater recharge ranged from the mid 1980s near the water table to the late 1970s for water collected at a depth of 31 m below the water table. Groundwater from sites beneath and hydraulically downgradient from the lake had CFC-modeled recharge dates that ranged from 1974 near the water table to 1955–1960 for water collected at a depth of about 28 m below the water table (2PNB-FL). The oldest groundwater recharge dates, obtained using CFCs, correlate with a bomb pulse ^3H concentration in groundwater (20.7 tritium units) that serves as a marker for water that was recharged during the late 1950s to the early 1960s. The older age of water collected from a depth of 28 m (2PNB-FL) below the water table, compared to water from a similar depth below the water table on the upgradient side of the lake (1PNB-FL), is indicative of the longer residence time of water along its flow path. Where sulfate-reducing and methanogenic zones exist in the aquifer systems, CFC-11 modeled recharge dates were consistently earlier than recharge dates based on the concentrations of CFC-12 or CFC-113. This indicates that concentrations of CFC-11 are being reduced and, therefore, the use of CFC-11 as a dating tool in these anaerobic zones is not precise.

Rates of groundwater flow estimated from CFCs and ^3H were used to estimate vertical hydraulic conductivity ($K_{v(\text{calc})}$) for the surficial aquifer and the intermediate confining unit at the 1PNB site. $K_{v(\text{calc})}$ ranged from 0.08 to 0.28 m/d for the surficial aquifer using porosity values of 0.25–0.40 and incorporating the uncertainty in the CFC-12 modeled recharge dates. For the intermediate confining unit, $K_{v(\text{calc})}$ ranged from 0.016 to 0.048 m/d using the range in porosity values and CFC-12 modeled recharge dates. Values of K_v that were used in the groundwater flow model were 0.6 and 0.09 m/d for the surficial aquifer and the intermediate confining unit, respec-

tively. Estimated values of K_v for the lake sediments, using the age of water at MLW-4 (calculated from the CFC-12 modeled recharge date) ranged from 0.011 to 0.023 m/d, with an average K_v of 0.019 m/d. The $K_{v(\text{calc})}$ of lake sediments is approximately an order of magnitude less than the $K_{v(\text{calc})}$ for the intermediate confining unit and about an order of magnitude greater than values used in the groundwater flow model (0.0018–0.0045 m/d). The consistency of K_v values between the two sources of data indicates that CFC-modeled recharge dates can be used in conjunction with other aquifer properties such as porosity and hydraulic head data to calculate the vertical or horizontal conductivity of shallow aquifers and confining units. Uncertainties in hydraulic head change, porosity, and age of water most likely would introduce less than an order of magnitude of error in calculating the hydraulic conductivity values.

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E. Busenberg and L. N. Plummer, U.S. Geological Survey, 432 National Center, 12201 Sunrise Valley Drive, Reston, VA 22092.

B. G. Katz, U.S. Geological Survey, 227 North Bronough Street, Suite 3015, Tallahassee, FL 32301.

T. M. Lee, U.S. Geological Survey, 4710 Eisenhower Boulevard, Suite B-5, Tampa, FL 33634.